

DESULFURIZATION AND SULFIDATION OF COAL AND COAL CHAR

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Part I: Desulfurization of Coal and Coal Char at Various Temperatures and Pressures

Introduction

This work was undertaken to obtain a better understanding of the desulfurization of Illinois No. 6 coal and of char derived therefrom. In particular, the effect of temperature, pressure, and methane content of the gas on the rate of sulfur removal and the final sulfur content of the product was studied.

The desulfurization of high-sulfur coals, cokes, and chars has been the subject of many investigations in the past, those pertaining to the desulfurization of coke going back as far as the 1850's. In recent times the subject has gained importance because of the necessity of utilizing large reserves of high-sulfur coal and of reducing the emission of sulfur-bearing gases in plants using coal or coke.

Experimental

Illinois No. 6 coal or char derived therefrom was used in all experiments; the size of the particles was between 12 and 18 mesh (average particle diameter ≈ 1.3 mm). The coal was dried for 24 hours at 110°C before it was used. Two types of char were prepared by treating the dried coals in H_2 for 3 hours at 600 or 800°C. The total sulfur content and the amounts of the various forms of sulfur present in the coal and the char (prepared at 600°C) are given in Table I.

The desulfurization experiments, using either dried coal or one of the chars, were done in H_2 , He, CH_4 , and mixtures of H_2 and CH_4 for periods of time up to 3 hours at 600 and 800°C at pressures up to 10 atm. For each experiment 100 to 250 mg of sample, contained in a platinum or nickel basket, was suspended in the hot zone of a resistance furnace. The gas flow rate was 0.5 l(STP)/min in all cases. The samples were lowered into and pulled out of the hot zone as quickly as possible under a flow of He. At the end of an experiment the entire sample was analyzed for total sulfur by means of the combustion method(1).

In selected cases surface-area measurements on partially desulfurized samples were made using the BET method. Use was also

made of electron-probe analysis and optical microscopy, in particular in those cases where the form of the sulfur was of interest.

Results and Discussion

The results for the desulfurization of dried coal in H_2 , CH_4 , and He at 600 and 800°C are shown in Figures 1 and 2. In all cases a rapid loss of sulfur during the first 30 minutes is observed. This initial rapid desulfurization is due partly to the reduction of pyrite (FeS_2) to pyrrhotite (FeS) and partly to the loss of less stable organic sulfur.

The coal originally contained 0.52 percent sulfur as pyrite (Table I), present as particles with an average diameter 1 to 50 μ . Typical pyrite particles, as observed in the dry coal, are shown in Figure 3a and b. Electron-probe analysis showed that these particles have a composition approaching that of FeS_2 (Figure 3c).

The partial pressure of sulfur in equilibrium with FeS_2 and FeS is 1 atm at 690°C(2). Therefore, some decomposition of pyrite into pyrrhotite is expected in an inert atmosphere at 600°C. This is shown in Figure 3d, e, and f for a coal which was treated for 10 min in He at 600°C. The composition of the large porous particle in Figure 3d was found to be close to that of pyrrhotite, as shown by Figure 3e, whereas the two smaller particles in Figure 3d had a composition between pyrite and pyrrhotite (Figure 3f).

Figure 3g is a micrograph of char prepared at 600°C, the chemical analysis of which is shown in Table I. This char served as the starting material for subsequent desulfurization experiments. The porous particles, in the center of the micrograph, are pyrrhotite formed by the complete reduction of pyrite, as evidenced by the x-ray spectrum in Figure 3h. This observation is in keeping with the chemical analysis in Table I which showed that no pyritic sulfur was present in this char.

It is interesting to note that the observed gasification in CH_4 is the same at 600 and 800°C, whereas in He or H_2 the gasification is about 20 percent higher at 800°C than at 600°C. It is generally accepted that the carbonization of coal takes place in two stages(3). In the temperature range 350 to 550°C the so-called primary devolatilization (not involving CH_4) takes place. The secondary gasification, involving mainly the release of CH_4 and H_2 , begins at about 700°C. In the presence of CH_4 , secondary gasification is therefore inhibited at 800°C and involves mainly the primary devolatilization equal to that observed at 600°C.

Although two types of char were used in the desulfurization experiments, only the experimental results pertaining to the char prepared at 600°C are presented here. The results obtained for the

char prepared at 800°C are similar and will not be presented in detail.

The effect of pressure and composition of the H_2 - CH_4 mixture and temperature on the rate of desulfurization of char, prepared at 600°C, is shown in Figures 4 to 6. Lower sulfur contents and higher rates of desulfurization are favored by an increase in PH_2 and temperature. The presence of CH_4 inhibits desulfurization.

In gas mixtures containing more than 25 percent CH_4 , gasification ceased after about 30 min of reaction time to reach a plateau (Figure 5). The gasification corresponding to this plateau is shown as a function of the percentage of CH_4 in the gas in Figure 7. For the char prepared at 600°C, gasification during desulfurization at 800°C (T_g) decreased considerably with increasing CH_4 percentage in the gas. Gasification for the char prepared at 800°C was only slightly dependent on the amount of CH_4 in the gas, irrespective of the temperature of desulfurization.

As seen from these results, desulfurization of coal char takes place in two distinct stages. The first stage shows a simultaneous rapid desulfurization and gasification. During the second stage sulfur is removed more slowly, practically independent of the extent of any further gasification. The observed initial rapid loss of sulfur together with the initial rapid gasification suggests that there may exist a relationship between the initial fractional removal of sulfur, $(\Delta S/S_0)_i$, and that of carbon, $(\Delta C/C_0)_i$.

The data in Figure 8 show the relative sulfur removal after about 15 minutes reaction time as a function of the relative carbon loss incurred during this time. A similar relationship was observed for the char prepared at 800°C. It is seen from Figure 8 that for each desulfurization temperature (T_g) the data points corresponding to various experimental conditions (e.g., total pressure, CH_4 content) form a curve, indicating a relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$.

Further examination of the data in Figure 8 shows that the same functional relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$ exists, irrespective of the temperature at which desulfurization took place. This is shown in Figure 9 where the open circles represent all the data points in Figure 8. Also shown in Figure 9 are the results obtained for the char prepared at 800°C, which show a similar relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$; however, the slope is steeper than observed for the char prepared at 600°C. The higher the char preparation temperature, the more gasification and desulfurization has taken place during charring. Therefore, it should not be concluded that it is generally more advantageous to use a char, prepared at a higher temperature, for subsequent desulfurization.

Also included in Figure 9 are the data from Jones, et. al. (4) who desulfurized a char derived from Illinois No. 6 coal,

prepared at 870°C. The desulfurization temperature varied between 704 and 1010°C, the pressure between 1 and ~8 atm, and they used H₂ as well as equimolar mixtures of H₂ and CH₄. Although their data show some scatter, it is concluded that there exists a relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$. The data of Batchelor et. al.(5) who used a char, prepared at 500°C, from a Pittsburgh seam coal, are also shown in Figure 9. Desulfurization took place in H₂-H₂S mixtures (pH₂ between 1 and 11 atm) at temperatures varying between 650 and 880°C. Also for these data, a relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$ is observed. It may thus be concluded that the functional relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$ is dependent only on the temperature at which the char was prepared. Subsequent desulfurization of a given char can only be achieved at the expense of loss in carbon, the extent of which is determined by the appropriate functional relationship depicted in Figure 9.

After the initial rapid drop in sulfur content of the char, a more gradual decrease is observed, Figures 4 to 6. Assuming that for this stage of the process the desulfurization reaction may be described by a first-order reaction relative to the sulfur content of the char, then

$$\frac{dS}{dt} = -k_S S \quad 1)$$

where S is the concentration of sulfur at time t and k_S a rate constant. Integration of Equation 1 gives

$$\log \frac{S}{S_0} = -k_S t \quad 2)$$

where S₀ is the sulfur concentration after 15 minutes of reaction time, after which desulfurization proceeds more gradually.

Because of the scatter in the experimental results, it was not considered warranted to treat the results obtained for the two chars separately. Figure 10, depicting the first-order plots, therefore represents the averages for both types of char. It is seen that log(S/S₀) is a linear function of time within the scatter of the data.

The rate constant k_S, obtained from the slopes of the lines in Figure 10, is shown in Figure 11A as a function of the concentration of H₂ in the H₂-CH₄ mixture for the desulfurization experiments at 5 atm pressure at 600 and 800°C. Although the equilibrium concentrations of CH₄ in H₂-CH₄ mixtures at 5 atm pressure are 56 percent and 16 percent at 600 and 800°C, respectively(2), no measurable weight increase of the char was recorded after treatment in CH₄ at 800°C. This indicates that CH₄ did not dissociate to any measurable extent under the present experimental conditions. Therefore, it may be assumed that the partial pressure of H₂ prevailing during the desulfurization experiments in H₂-CH₄ mixtures was the same as that in the ingoing mixture.

On this basis, Figure 11B was plotted, supplemented with some data obtained from desulfurization experiments in 100 percent H_2 at 1 and 5 atm pressure. It is seen that the rate constant pertaining to the second stage of desulfurization in 100 percent H_2 is the same as that in H_2 - CH_4 mixtures, although in 100 percent H_2 gasification continues in the second stage (Figures 4 to 6). This suggests that desulfurization and gasification are interrelated in the initial stages only; in the second stage desulfurization takes place at a rate independent of gasification.

To explain these observations, it is suggested that the initial loss of carbon—which is accompanied by a simultaneous loss of (mainly organically bound) sulfur—creates new pores providing better access for the reducing gas to the pyrrhotite particles embedded in the char. This is supported by the observed change in surface area of the char during desulfurization. The initial surface area of char prepared at $600^\circ C$ is about $2\text{ m}^2/\text{g}$. The change in surface area is most pronounced during the first hour of desulfurization, particularly at $800^\circ C$, Figure 12. The pore surface area increases with increasing temperature and pressure and, hence, the amount of gasification.

A char, prepared at $600^\circ C$ and subsequently desulfurized for 2 hours in 5 atm H_2 at $800^\circ C$, was analyzed for the various forms of sulfur present in the product. The analysis showed that of the total sulfur content of 0.16 percent, about 0.11 percent was present as pyrrhotite and about 0.05 percent as organic sulfur. The micrograph in Figure 13a for this partially desulfurized product shows three types of particles: bright, greyish colored, and two-phase particles partly bright and partly grey. The composition of the greyish particles varies somewhat but nominally approaches that of pyrrhotite (Figure 13b and c). The bright particles are iron (Figure 13d) formed by the complete reduction of pyrrhotite.

It is concluded from these observations that most of the sulfur is in the form of pyrrhotite during the later stages of desulfurization. The overall rate of desulfurization during this stage is thus expected to be mainly governed by the slow reduction(6) of pyrrhotite in H_2 .

Conclusions

It was found that the desulfurization of coal char in mixtures of H_2 and CH_4 takes place in two distinct stages. In the first stage rapid desulfurization is accompanied by gasification. These two processes were shown to be interrelated, the relationship being dependent on the char preparation temperature only. The second stage of desulfurization was found to proceed at a much slower rate and is being controlled by the slow reduction of pyrrhotite to iron.

References: listed at end of part II.

Table I

Forms of Sulfur (in Wt.%) Present in Dried
Coal and Char Derived Therefrom (3h, H₂, 600°C)

<u>Form of Sulfur</u>	<u>Dried Coal</u>	<u>Coal Char</u>
Pyrite	0.53	-
Sulphate	0.12	0.005
Sulphide	0.005	0.13
Organic	1.27	0.61
Total	1.93	0.75

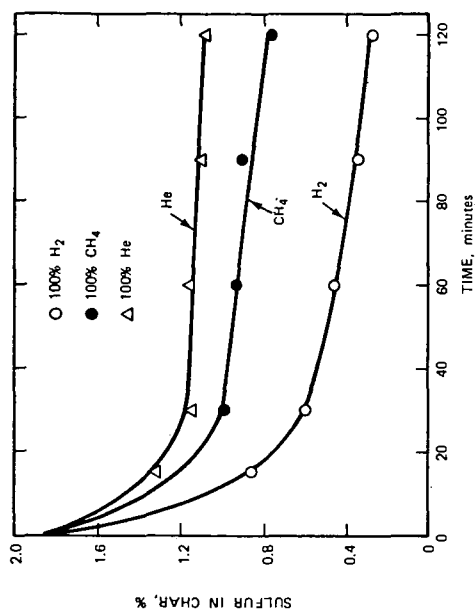
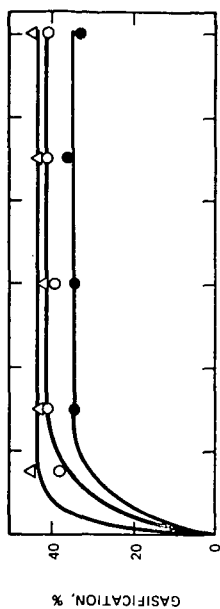


Figure 2. DESULFURIZATION AND GASIFICATION OF DRIED ILLINOIS #6 COAL IN H_2 , CH_4 , AND He AT 800°C AND 1 ATM PRESSURE

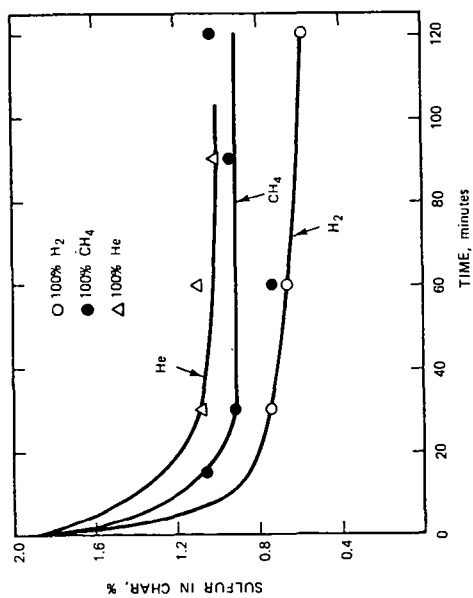
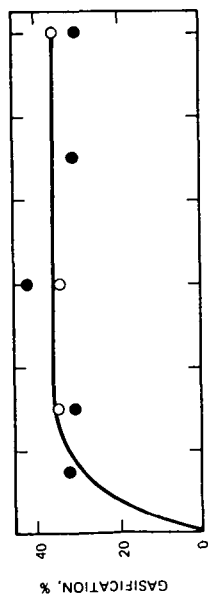


Figure 1. DESULFURIZATION AND GASIFICATION OF DRIED ILLINOIS #6 COAL IN H_2 , CH_4 , AND He AT 600°C AND 1 ATM PRESSURE

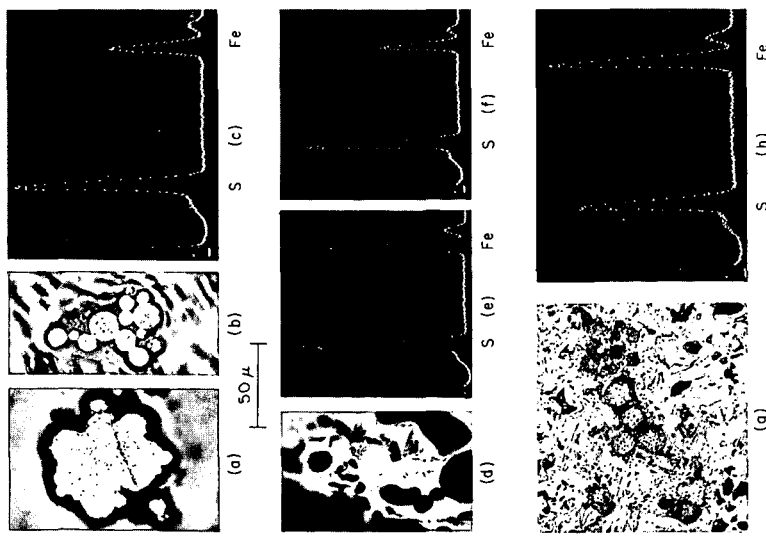


Figure 3. MICROGRAPHS AND ELECTRON PROBE ANALYSIS FOR COAL AND CHAR
 TOP: ORIGINAL DRY COAL;
 MIDDLE: COAL TREATED IN He AT 600°C FOR 10 MIN;
 BOTTOM: CHAR (3 h IN H₂ AT 600°C).

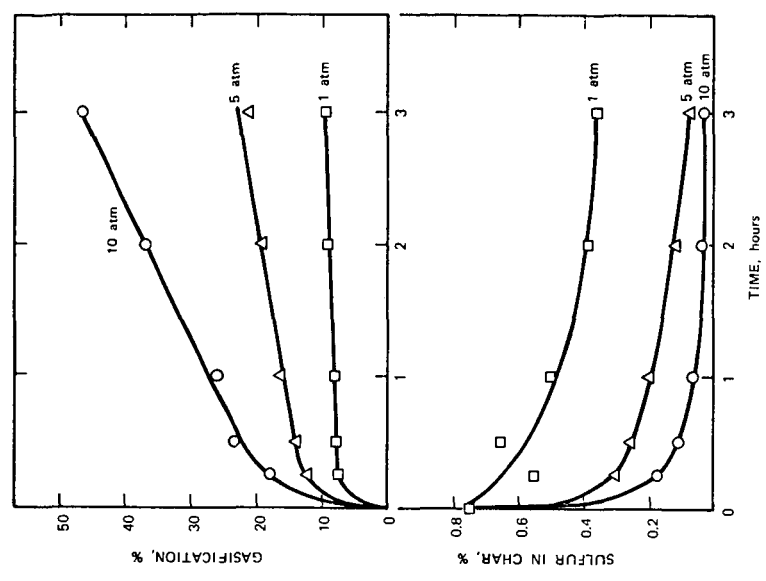


Figure 4. DESULFURIZATION AND GASIFICATION OF ILLINOIS CHAR
 (PREPARED AT 600°C) IN H₂ AT INDICATED PRESSURES
 AT 800°C

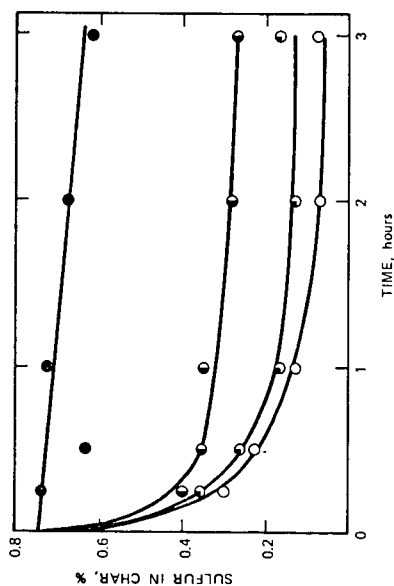
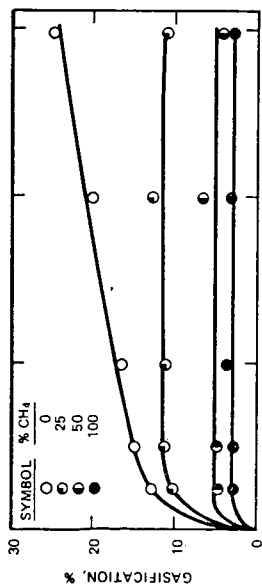


Figure 5. DESULFURIZATION AND GASIFICATION OF ILLINOIS CHAR (PREPARED AT 600°C) IN $\text{H}_2\text{-CH}_4$ GAS MIXTURES OF 5 ATM AT 800°C

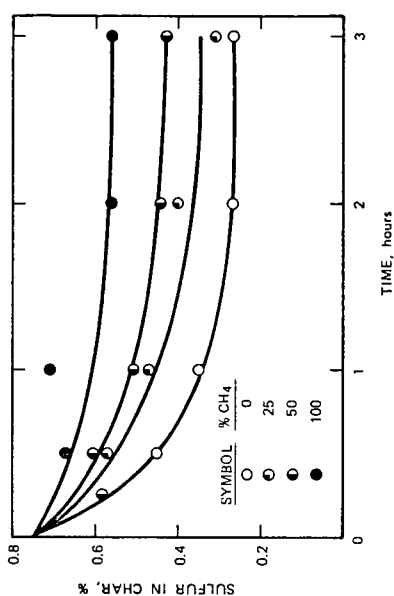
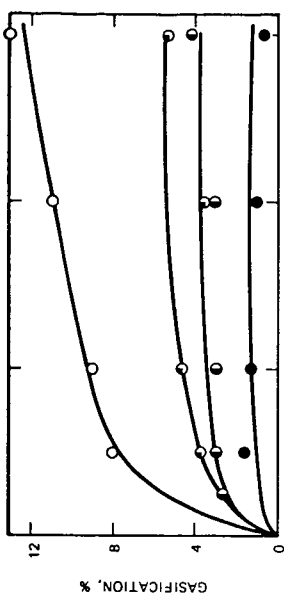


Figure 6. DESULFURIZATION AND GASIFICATION OF ILLINOIS CHAR (PREPARED AT 600°C) IN $\text{H}_2\text{-CH}_4$ MIXTURES OF 5 ATM AT 600°C

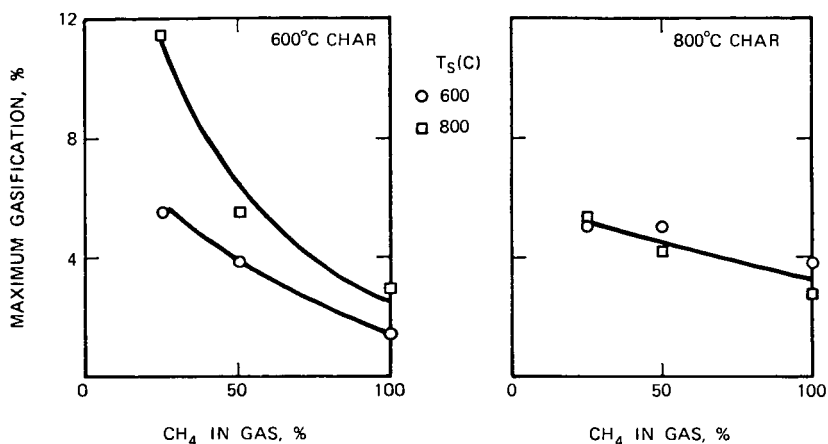


Figure 7. FINAL LEVEL OF GASIFICATION AS A FUNCTION OF THE AMOUNT OF CH₄ IN H₂-CH₄ MIXTURES FOR TWO TYPES OF CHAR, DURING DESULFURIZATION AT 600 AND 800°C (T_S)

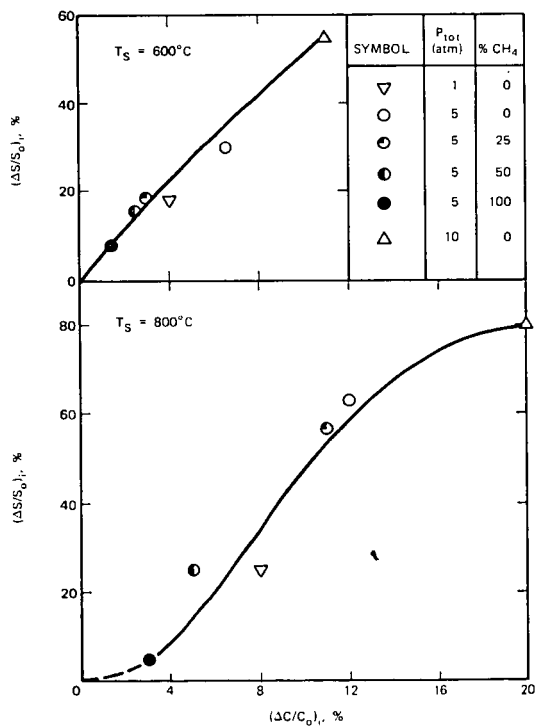


Figure 8. RELATION BETWEEN INITIAL LOSS OF SULFUR AND CARBON (AFTER 15 MINUTES REACTION TIME) FOR A CHAR PREPARED AT 600°C AND SUBSEQUENTLY DESULFURIZED UNDER INDICATED CONDITIONS AT T_S = 600 OR 800°C

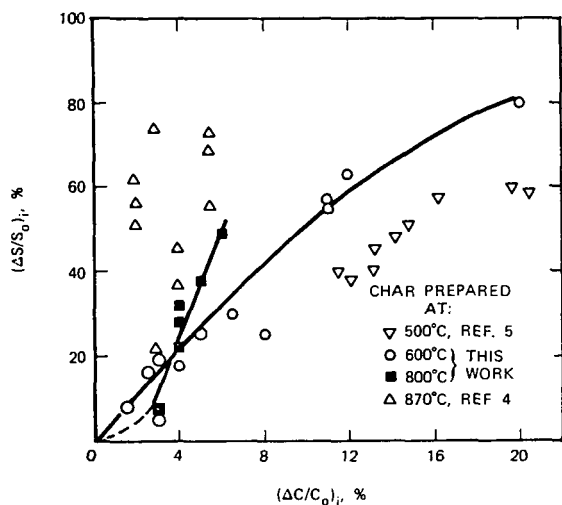


Figure 9. GENERAL RELATIONSHIP BETWEEN INITIAL LOSS OF SULFUR AND CARBON FOR TWO TYPES OF CHAR, SHOWING THAT THE DATA FOR VARIOUS EXPERIMENTAL CONDITIONS FOR A GIVEN CHAR ARE REPRESENTED BY THE SAME FUNCTION

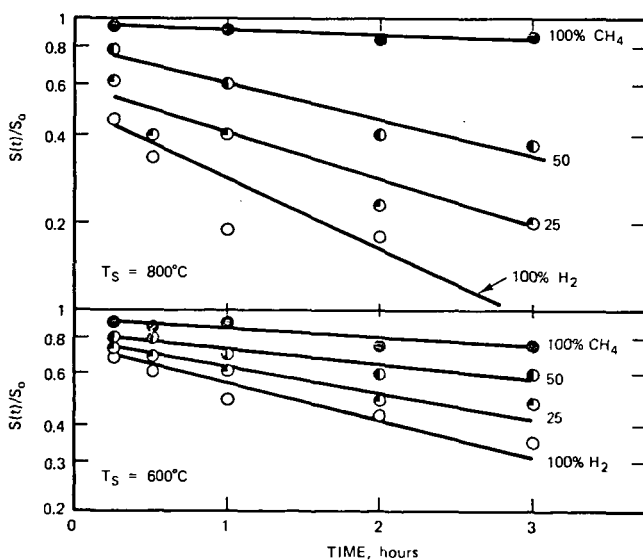


Figure 10. DESULFURIZATION OF CHAR IN MIXTURES OF H_2 AND CH_4 AT 5 ATM AND INDICATED TEMPERATURES, AS A FIRST-ORDER REACTION

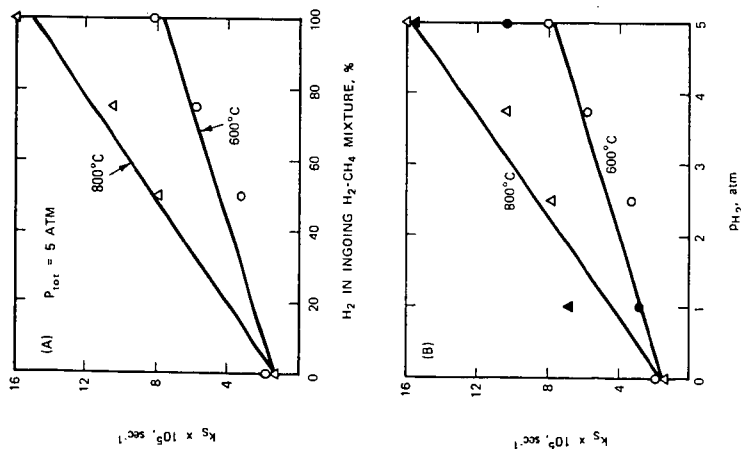


Figure 11. FIRST-ORDER RATE CONSTANTS FOR DESULFURIZATION AT INDICATED TEMPERATURES SHOWN AS A FUNCTION OF (A) H_2 CONTENT OF GAS MIXTURE (5 ATM) (B) PARTIAL PRESSURE OF H_2 (5 ATM) (SOLID SYMBOLS REPRESENT DATA FOR 100% H_2)

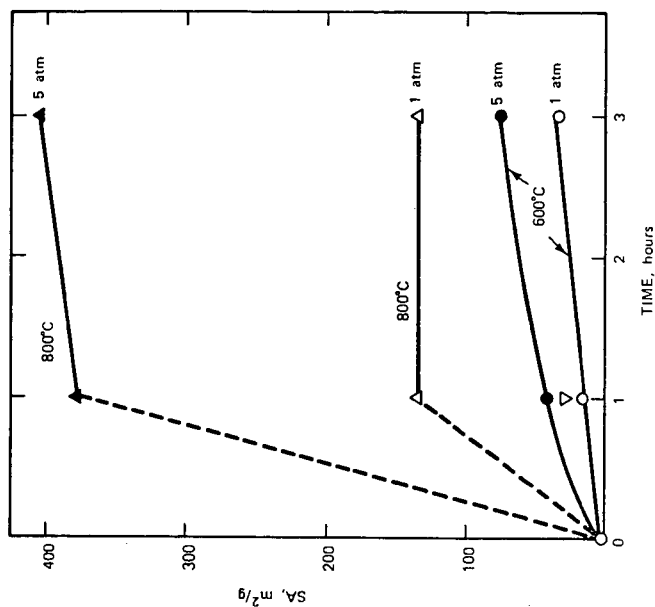


Figure 12. SURFACE AREA (SA) OF CHAR AFTER TREATMENT IN H_2 AT INDICATED TEMPERATURES AND PRESSURES

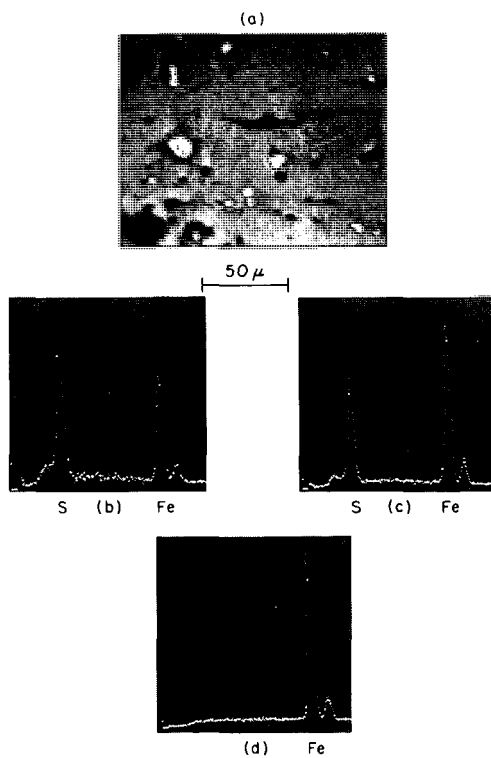


Figure 13. OPTICAL MICROGRAPH AND ELECTRON ANALYSIS OF CHAR,
TREATED IN $p_{H_2} = 5$ atm, 800°C FOR 2 HOURS, SHOWING
THE PRESENCE OF PYRRHOTITE AND REDUCED IRON